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CATALYST DEVELOPMENT FOR THE SELECTIVE METHYLATION OF CATECHOL

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Abstract - Gas-phase alkylation of catechol with methanol on γ-alumina and modified γ-alumina catalysts is studied experimentally. By limiting the conversion to $X < 0.3$, the formation of polymethylated species can be avoided and only the three isomers guaiacol, 3-methylcatechol and 4-methylcatechol are observed. Optimising the catalyst composition and the reaction conditions, a selectivity of 0.75 for the industrially most valuable product 3-methylcatechol can be obtained.

INTRODUCTION

Synthesis of alkylcatechols is an important process in fine chemicals production. These substances are widely used in the synthesis of flavouring agents, agricultural chemicals and pharmaceuticals (Fiege et al., 1991). Previously γ-Al_2O_3 was found to be an effective catalyst for the gas-phase methylation of catechol with methanol as methylation agent (Porchet et al., 1993). The reaction leads to many different alkylated products. The reaction conditions have been optimised to avoid the formation of polymethylated products.

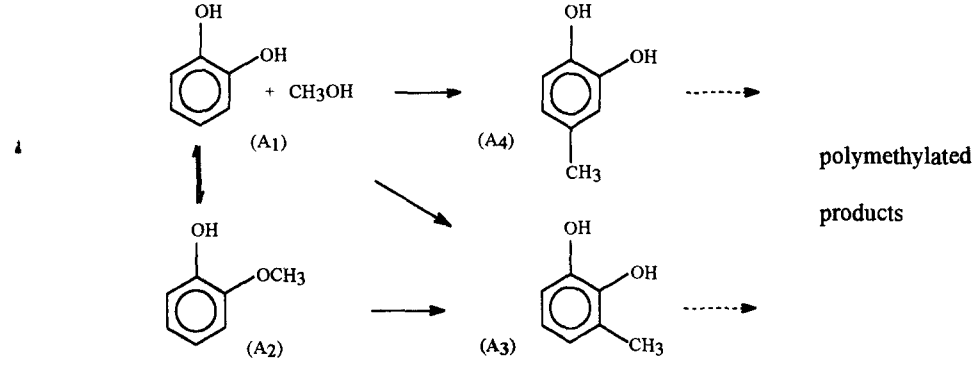

Fig.1 Reaction scheme of catechol methylation

The three primary products are guaiacol (A_2), 3-methylcatechol (A_3), 4-methylcatechol (A_4); they are formed by primary methylation of catechol (A_1). At low conversion and in the temperature range of 260-310°C, the oxygen-alkylation is favoured, e. g. the main product is guaiacol. The carbon-alkylation is mainly ortho-selective.

Previous studies of phenol alkylation with methanol showed that this type of reaction is very sensitive to the acidic and basic properties of the catalyst surface (Tanabe et al., 1976; Velu et al., 1994). Different metal ions as Ca^{2+}, K^+, Li^+, Mg^{2+} or ions as B^{3+} and F^- are added to γ-alumina in order to modify these surface properties (Lercher et al., 1984; Berteau et al., 1987, 1989; Jurczyk et al., 1989). The purpose of this work is to increase the selectivity for the 3-methylcatechol through a catalyst modification.

EXPERIMENTAL

Catalysts preparation

Pure γ-alumina (Al-3982, Engelhard, NL) is used as starting material. The modified catalysts are prepared by wet capillary impregnation with aqueous solutions of nitrate salts. H_3BO_3 and NH_4F solutions are used in the case of B^{3+} and F^- impregnation.

The concentration of the solutions are adjusted to get the required ratio ion /Al^{3+} (atomic-%) by varying the amount of nitrates added to γ-alumina. Before impregnation, γ-alumina is dried at 200°C for 2 hours. After 8 hours at 50°C the impregnated samples are calcinated in air during 8 hours at 620°C.

Apparatus and catalytic test

The reactants are premixed with water and the solutions are fed into the evaporator using a micro-feed pump. The catalytic reaction is carried out in the temperature range of 260-310°C and at 101.3 kPa in a stainless steel tubular fixed-bed reactor (Fig. 2). To change the residence time in the reactor, the molar inlet flow (F_0) and the catalyst mass (m_{cat}) are varied in the range of $5 \cdot 10^{-2} < F_0 < 10$ mol·h^{-1} and $2 \cdot 10^{-2} < m_{cat} < 3 \cdot 10^{-1}$ kg.

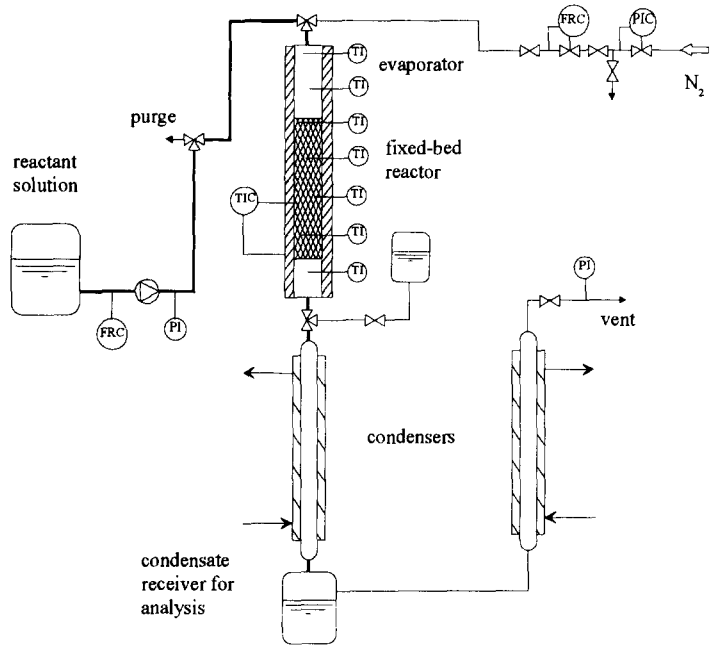

Fig. 2 Schematic layout of the experimental apparatus

The reaction mixture is condensed at the reactor outlet and collected for analysis. The product distribution is determined quantitatively by HPLC: the separation is accomplished at room temperature on a Nucleosil 5 C_{18} column (mobile phase CH_3CN:H_2O = 1:9 molar ratio, flow rate = 1 ml·min^{-1}, operating pressure = 18 MPa). The signals are observed with UV detection at λ = 270 nm.

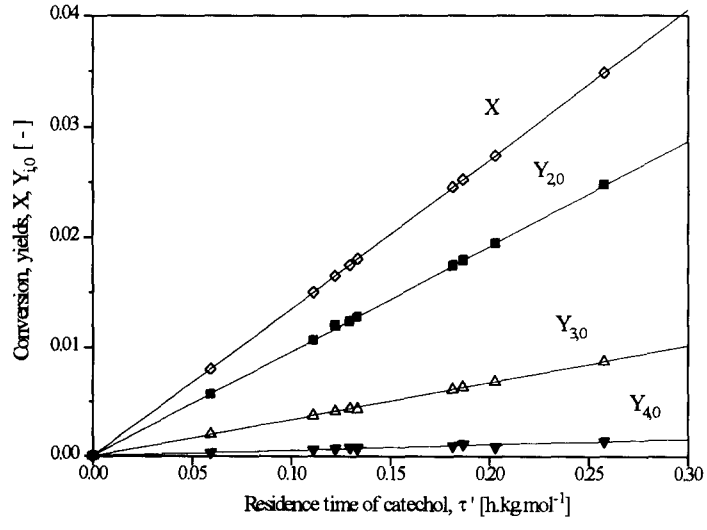

Fig.3 Differential conversion and yields on γ-alumina after initial deactivation; temperature = 270°C, $P_{1,0}$ = 12.7 kPa, $P_{5,0}$ = 12.7 kPa, $P_{6,0}$ = 76.0 kPa

To test the different catalysts, the reaction is restricted to the primary methylation: catechol conversion is limited to values of $X < 0.05$ allowing the reaction to be carried out in the differential kinetic region (Fig. 3). The standard reactants feed is a solution with a molar ratio catechol : methanol : water = 1: 1: 6 that corresponds to initial partial pressures of 12.7 kPa for each reactant and 76.0 kPa for water. The initial reaction rate of catechol ($-R_{10}$) is measured under steady-state conditions after 8-10 hours of the catalyst activity stabilisation and is used to compare the catalysts activity. The differential selectivities ($s_{i,0}$) for the monomethylated products (under steady-state conditions) are used to compare the different catalysts:

$$s_{i,0} = \frac{R_{i0}}{-R_{10}} \cong \frac{Y_{i,0}/\tau'}{X/\tau'} = \frac{Y_{i,0}}{X} \qquad i=2,3,4 \qquad \text{where } \tau' = \frac{m_{cat}}{F_{10}}$$

RESULTS

The specific surface areas of the studied catalysts are listed in Table 1. Pure γ-alumina exhibits a B.E.T. surface area of 165 $m^2 \cdot g^{-1}$. The surface areas remain almost unchanged after incorporation of B^{3+}, Li^+ and Mg^{2+} with 5% of ion content (atomic-%) but decrease in the case of Ca^{2+} and K^+. A reduction of this area is also observed with higher Mg^{2+}-content: the pore size distribution shows a small decrease of the average mesoporous diameter for modified γ-alumina and a global decrease of all diameters with ion content higher than 7.5%.

Table 1
Characteristics of the different catalysts

Catalyst	Ion content (atomic - %)	Specific B.E.T. area ($m^2 \cdot g^{-1}$)	Initial rate $-R_{10}$ ($mol \cdot kg^{-1} \cdot h^{-1}$)	Differential selectivities (-) $s_{2,0}$	$s_{3,0}$	$s_{4,0}$
γ-Al_2O_3	-	165	0.135	0.71	0.26	0.03
F^- / γ-Al_2O_3	7.5	144	0.132	0.70	0.25	0.05
B^{3+} / γ-Al_2O_3	5	171	0.144	0.75	0.24	0.01
Ca^{2+} / γ-Al_2O_3	5	146	0.006	0.74	0.24	0.02
K^+ / γ-Al_2O_3	5	150	0.001	0.70	0.25	0.05
Li^+ / γ-Al_2O_3	5	171	0.055	0.60	0.39	0.01
Mg^{2+} / γ-Al_2O_3	5	167	0.113	0.34	0.62	0.04
Mg^{2+} / γ-Al_2O_3	7.5	156	0.092	0.30	0.66	0.04
Mg^{2+} / γ-Al_2O_3	10	140	0.043	0.53	0.44	0.03

Differential reactor: catalyst screening

After a stabilisation period of 8-10 hours, activity of γ-alumina and modified γ-alumina catalysts remains constant. The catalytic activity, expressed by the initial reaction rate ($-R_{10}$), and the differential selectivities ($s_{i,0}$) on pure γ-alumina and on various modified catalysts at 270°C (Table 1). Catalysts modified with F^-, B^{3+}, C^{2+} and K^+ exhibit the same product selectivities as pure γ-Al_2O_3 whereas their activity is decreased. This lost of activity depends on the ion type used and is particularly severe for Ca^{2+} and K^+.

With Li^+-modified catalysts, a remarkable selectivity increase for the desired 3-methylcatechol is observed. But the most significant change is obtained with Mg^{2+}-modified catalysts: the differential selectivity $s_{3,0}$ can be improved up to 0.65.

Deactivation

Under differential conditions pure γ-alumina and F^-, B^{3+}, Ca^{2+}, K^+ and Li^+-modified catalysts deactivate without influencing the differential selectivities. In the case of Mg^{2+}-modified catalysts, it is interesting to notice that the differential selectivities change during the first hours on stream (Fig. 4): the selectivity for 3-methylcatechol increases while the relative formation of guaiacol is reduced. The effect of this pre-treatment, which is always favourable to the desired product, is more or less important depending on Mg^{2+} content.

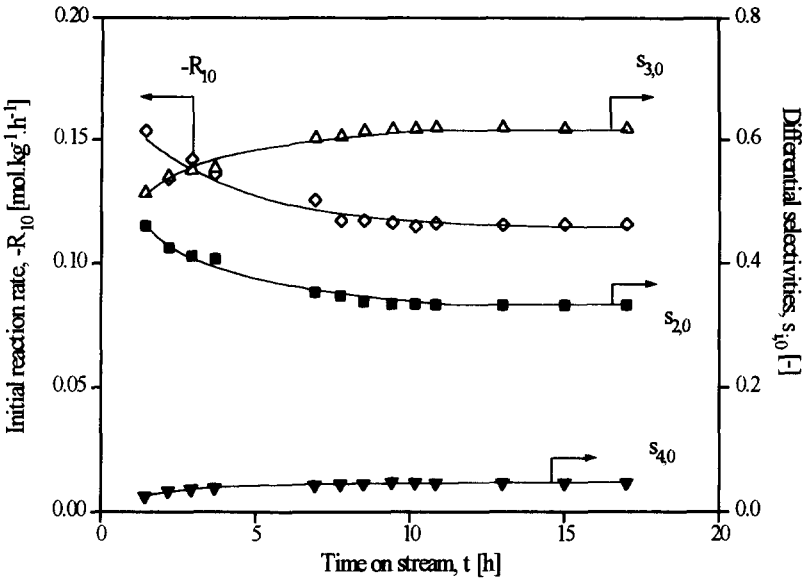

Fig.4. Deactivation of Mg^{2+} / γ-Al_2O_3 (5 %) catalyst; temperature = 270°C, $P_{1,0}$ = 12.7 kPa, $P_{5,0}$ = 12.7 kPa, $P_{6,0}$ = 76.0 kPa, τ' = 0.38 h·kg·mol^{-1}

Catalysts modified with Mg^{2+}

Mg^{2+}-modified γ-alumina is of particular interest due to the fact that 3-methylcatechol selectivity increases with respect to pure γ-alumina without big lost of catalytic activity (table 1). The selectivity $s_{3,0}$ is strongly dependent on the Mg^{2+}-content (Fig. 5). In the concentration range of 5-7.5% of Mg^{2+}, it passes through a maximum of $s_{3,0}$ = 0.65 and 3-methylcatechol becomes the main product under differential conditions. It is worthwhile to note that only the relative formations of guaiacol and 3-methylcatechol are affected by the percentage of Mg^{2+} added to γ-alumina: the oxygen-alkylation is reduced in favour of carbon-alkylation, but the ring methylation stays largely ortho-selective. The behaviour of these Mg^{2+}-modified catalysts is very sensitive to the purity of the reactants.

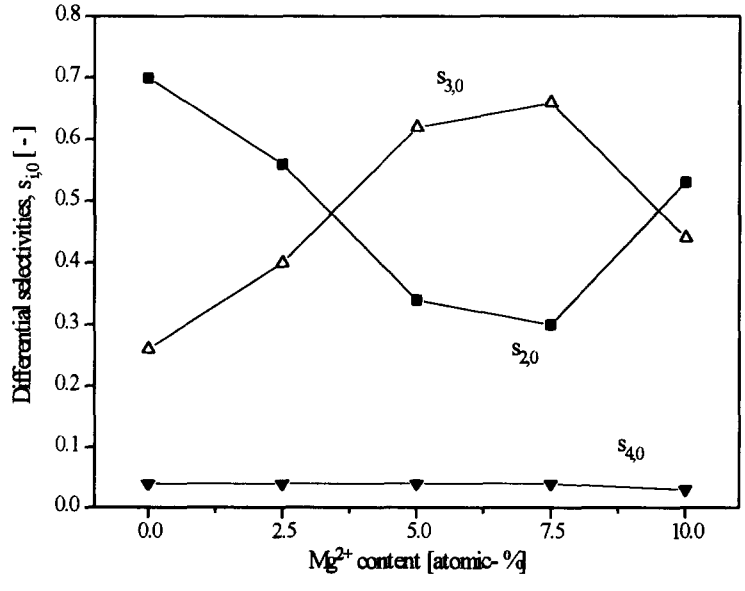

Fig.5 Differential selectivities of the monomethylated products as function of Mg^{2+} added to γ-Al_2O_3; temperature = 270°C, $P_{1,0}$ = 12.7 kPa, $P_{5,0}$ = 12.7 kPa, $P_{6,0}$ = 76.0 kPa, τ' = 0.38 h·kg·mol^{-1}

Integral reactor

As presented in Fig. 1, the three monomethylated isomers are formed by direct alkylation of catechol with methanol. The formation rate of 4-methylcatechol is slow compared to the production rates of the other species which is favourable because it is an undesired stable product. On the other hand guaiacol is itself a methylation agent: it decomposes in a reverse reaction to catechol and methanol or can be transformed by rearrangement to the desired 3-methylcatechol (Porchet et al, 1994). Therefore the overall yield Y_2 shows the typical reaction path of an intermediate product. The yield of 3-methylcatechol increases with catechol conversion whereas the guaiacol yield passes a maximum value as shown for pure γ-alumina in Fig. 6.A). However the monomethylated products react with alkylation agents to form stable higher methylated species. The reaction has therefore to be stopped at an optimal conversion.

As the differential selectivity of 3-methylcatechol is considerably improved using Mg^{2+}-modified catalysts, the obtainable integral selectivity can be increased to values up to 0.75 for a catechol conversion of X = 0.28. This corresponds to a 150% higher yield compared to pure γ-alumina at the same conversion as shown in Fig. 6.b).

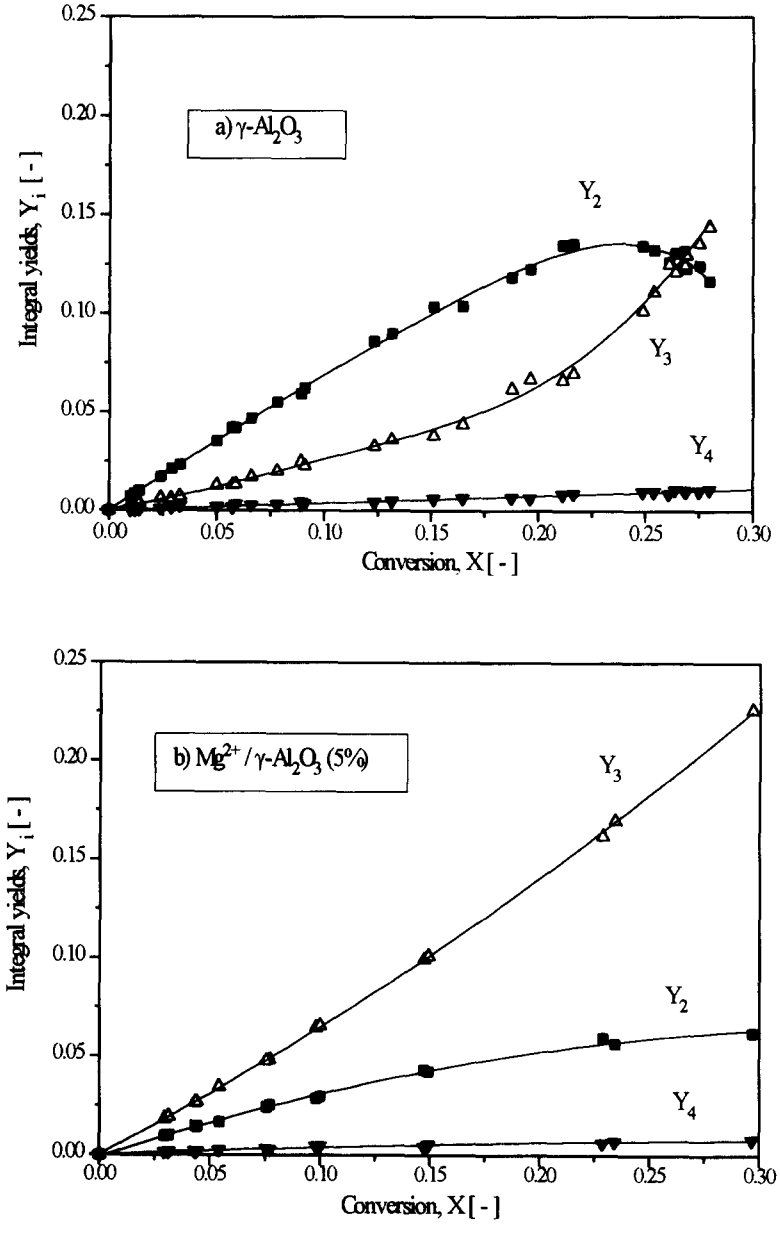

Fig. 6.a) & b) Integral yields of the three monomethylated products as function of catechol conversion; temperature: 262°C (a), 270°C (b), $P_{1,0}$ = 12.7 kPa, $P_{5,0}$ = 12.7 kPa, $P_{6,0}$ = 76.0 kPa, τ' = 0.3 - 5.7 h·kg·mol^{-1}

CONCLUSION

On pure γ-alumina the selectivity for the desired product 3-methylcatechol can be optimised taking into account the initial formation rates of the monomethylated compounds and the consecutive rearrangement of guaiacol. This leads to a selectivity $s_3 = 0.52$ at a conversion of $X = 0.28$. Guaiacol and catechol must then be separated and may be recycled.

It has been shown that the differential selectivity for 3-methylcatechol can be increased by modifying the catalyst with Mg^{2+}. This leads to a selectivity $s_3 = 0.75$ at the same conversion and it decreases the amount of guaiacol that has to be recycled.

ACKNOWLEDGEMENT

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NOMENCLATURE

F_0	total molar flow	$mol \cdot h^{-1}$
F_{10}	molar flow of catechol	$mol \cdot h^{-1}$
m_{cat}	catalyst mass	kg
$P_{i,0}$	initial partial pressure of i	kPa
R_{i0}	initial formation rate of i	$mol \cdot kg^{-1} \cdot h^{-1}$
$-R_{10}$	initial reaction rate of catechol	$mol \cdot kg^{-1} \cdot h^{-1}$
s_i	selectivity of i	-
$s_{i,0}$	differential selectivity of i	-
t	time on stream	h
τ'	residence time of catechol	$h \cdot kg \cdot mol^{-1}$
X	catechol conversion	-
Y_i	integral yield of i	-
$Y_{i,0}$	differential yield of i	-

indices i:

2	guaiacol
3	3-methylcatechol
4	4-methylcatechol
5	methanol
6	water

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